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Temperature and wavelength dependence of transient photoconductivity in ZnTe

S Johnston[1], R K Ahrenkiel[1], S Bhunia[2] and D N Bose[3]*

[1]National Renewable Energy Laboratory, Golden, Colorado-80401 USA

[2]Saha Institute of Nuclear Physics, 1/AF Bidhannagar, Kolkata-700 064, India

[3]University Science Instrumentation Centre, Calcutta University, Kolkata-700 009, India

E-mail tutubose@yahoo.co.in

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Abstract Transient photoconductivity studies have been carried out between 125-293 K on Zn-annealed *p*-ZnTe single crystals using a contactless rf technique with 532 nm laser pulse excitation. The samples had resistivity of 13.7 ohm-cm with hole concentration 8.42×10^{15}/cm^3 at 300 K. The decay was characterized by 2 decay times. The faster decay was found to increase from 1×10^{-6} s at 125 K to reach a maximum of 23×10^{-6} s at 250 K and then decrease to 20×10^{-6} s at 293 K. The decay times observed are attributed to carrier excitation from and trapping due to a shallow donor level at ~0.04 eV. When the excitation wavelength was varied from 532 nm to 592 nm, both the signal amplitude and the decay times increased, with surface effects being dominant at shorter wavelengths. The results are compared with steady-state photoconductivity measurements.

Keywords · Zinc telluride, transient photoconductivity, trapping

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1. Introduction

ZnTe is a II-VI compound semiconductor whose properties have not been studied as extensively as those of ZnSe and CdTe. It has a direct band-gap of 2.26 eV at 300 K with cubic zinc-blende structure (lattice constant of 6.1037 Å) [1] and, unlike other II-VI compounds, is generally *p*-type. Alloyed with other II-VI semiconductors, it is a promising material for a variety of optoelectronic devices in the visible and near ultraviolet optical ranges. Although the importance of ZnTe-based materials for these applications has been recognized, the difficulty in preparing *n*-type material with good conductivity has hampered progress in the past. Recently, breakthroughs have occurred in realizing low resistivity *n*-type doped ZnTe epitaxial layers [2]. Pure green light emitting diodes (LEDs) based on ZnTe have also been realized by various techniques [3].

Minority carriers play an important role in all such devices and hence their thorough understanding is crucial. Since the properties of the II-VI compounds are mostly dominated by point defects, knowledge of the behavior of carrier lifetimes with different defect modification processes, such as annealing under different conditions, are important.

Time-resolved photoconductivity measurements on 3 types of ZnTe were reported by Bose *et al* [4]. From the fast decay, the minority carrier lifetimes were found to be 4.6×10^{-8} s for as-grown, 3.2×10^{-7} s for Zn-annealed and 3.1×10^{-7} s for In-doped semi-insulating (SI) ZnTe. Here, we report the study of temperature dependence of transient photoconductivity observed on a longer time scale on Zn-annealed *p*-ZnTe. This decay is determined by carrier excitation from and trapping due to a shallow donor level at ~0.04 eV as discussed below.

2. Experimental

ZnTe was prepared by microwave synthesis from 7Ns purity elements followed by single crystal growth from a 4% Te-rich melt which resulted in the lowering of growth

*Corresponding Author

temperature from the melting point of ZnTe which is 1295°C to 1150°C Crystals were grown by very slow lowering of the quartz crucible by the Bridgman technique as described by Bhunia and Bose [5] resulting in growth along the <111> direction as determined by Laue photographs Samples were cut perpendicular to the growth axis and prepared by lapping and etching Resistivity and Hall effect studies were carried out between 120–300 K to determine the carrier concentration and mobility which were found to be 1.6×10^{16} cm^{-3} and 46 cm^2/V s in as-grown samples at 300 K Since the p-type nature of ZnTe is attributed to the predominant defects being Zn vacancies, annealing was carried out in a Zn atmosphere at 650°C for 12 hours which resulted in decrease in hole concentration to 8.42×10^{15}/cm^3, increase in hole mobility to 54 cm^2/V s and increase in resistivity from 8 5 ohm–cm to 13 7 ohm-cm The hole activation energy was found to be 149 meV for the Zn-annealed samples Cu_{Zn} is known to give an acceptor level at this energy and such a level was also detected in photoluminescence studies [6]

From optical absorption experiments, a plot of $(\alpha h\nu)^2$ *vs* $h\nu$ showed a direct band-gap of 2 26 eV at 300 K However, there was a long tail in the absorption edge extending to ~2 1-eV which is attributed to defects giving rise to shallow levels above the valence band This is important in explaining the wavelength dependence of photoconductive decay

Transient photoconductivity was studied using a contactless radio-frequency photoconductive decay technique as reported by Ahrenkiel *et al* [7] A pulsed light source derived from the second harmonic of a YAG laser at 532 nm was used to excite the sample The light pulse was strongly attenuated to provide energy of μJ/pulse The experimental technique uses an ultra-high frequency source (424 MHz) to induce phase-locked currents in the semiconducting sample These sample currents produce, in turn, an electromagnetic field that is proportional to the sample conductivity. The source also acts as a detector and measures the electromagnetic field produced by the sample. The distance between the source and the sample could be varied by an electrically driven micro-positioner so that the signal from the sample-dark-conductivity remained constant The coupling was adjusted so that the detector produced a fixed signal irrespective of sample size and dark conductivity This signal was directed to a high-frequency bridge circuit and the system coupling varied until the dark response was balanced by a bridge circuit When operated over a frequency range between 420–430 MHz, the resonant detection system had a Q factor of over 200. The system rise-time is about 4 ns which is the minimum detectable lifetime.

3. Results

The transient photoconductive decays at 293 K were characterized by fast and slow components as shown in Figure 1 with excitation using a 532 nm laser pulse When the sample temperature was varied from 125 K to 293 K the slower transient in the Zn-annealed sample decay varied as shown in Figure 2 While the fast decay is attributed to a direct radiative recombination process, the slower decay is due to trap emission and capture from shallow traps. It is observed that the amplitude of the response increased with temperature as seen in Figure 2 while the decay time varied as shown in Figure 3 It increased slowly from 125 K to 210 K, rapidly till 250 K where it reached a maximum value of 22 5 μs and then decreased to 20 μs at 293 K

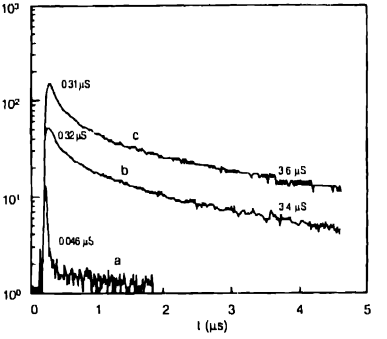

Figure 1. Transient photoconductivity of (a) as-grown ZnTe, (b) Zn-annealed ZnTe and (c) SI-ZnTe with laser excitation at λ = 532 nm

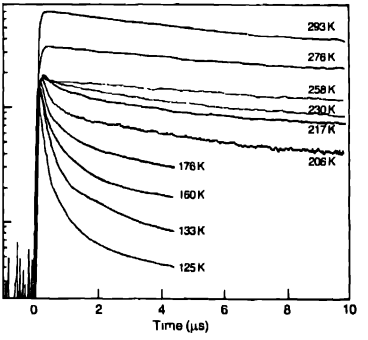

Figure 2. Transient photoconductivity in ZnTe between T = 125 –293 K (λ = 532 nm).

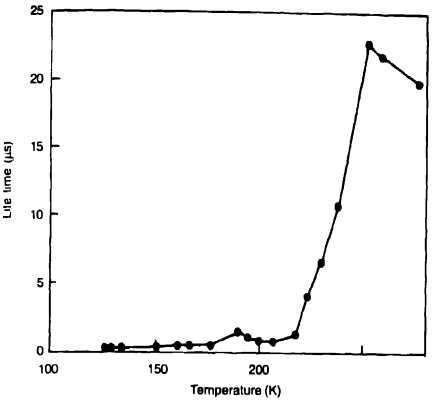

Figure 3. Variation of transient decay times with temperature (λ 532 nm)

When the incident wavelength was varied, the decay time increased with increasing wavelength Since the band-gap of ZnTe is 2 26 eV corresponding to λ = 549 nm, laser pulses at 532 nm wavelength resulted in strong absorption near the surface whereas at longer wavelengths, the incident radiation was able to penetrate into the bulk This resulted in surface recombination being important at shorter wavelengths while bulk recombination was dominant at longer wavelengths The decays are characterized by 2 time constants τ_1 and τ_2 whose values are given in Table 1

Table 1 Variation of transient decay times with incident laser wavelength

Wavelength λ nm) and photon energy (eV)	Max response (mV)	Decay time τ_1 (μs)	Decay time τ_2 (μs)
555 (2 234)	$1\ 5 \times 10^2$	5 543	–
585 (2 119)	$1\ 85 \times 10^2$	24 42	98 27
592 (2 095)	3.0×10^2	36 04	177 3
592 (low intensity)	$2\ 0 \times 10^2$	8 485	76 97

4. Discussion

While the fast decay in photoconductivity as observed in Figure 1 is due to direct electron-hole recombination, the slower decays with larger time constants are due to trapping and release of carriers from shallow traps. The earlier paper [4] focused on the fast decay times due to direct recombination from which the values of the recombination constant $B = 1.4 \times 10^{-9}$ cm^3 s^{-1} and 4×10^{-10} cm^3 s^{-1}, respectively were obtained for the two types of samples. The present results on the other hand, are concerned with the slower decays determined by traps This carrier trapping time constant τ_t is given by

$$1/\tau_t = \sigma\, v_{th} N_t,$$

where σ = capture cross section, v_{th} = thermal velocity of carriers = 10^7 cm/s and N_t = trap concentration For a decay time of 5 543 μs, if N_t is assumed to be 10^{14}/cm^3 then $\sigma = 1\ 68 \times 10^{-16}$/cm^2, a value characteristic of neutral traps. This assumes all the traps to be empty and available for capture of carriers At high injection levels, the concentration of empty traps becomes $(N_t - n)$ and hence, the capture rate decreases giving longer decay times This is observed from Table 1 when the pulse energy is varied at 592 nm

If the trap depth is E_t, the rate of release from traps is then obviously proportional to exp $(-E_t/kT)$ Thus, the rapid increase in free-carrier life-time between 210 K and 250 K is due to de-trapping or release of carriers from traps. Assuming that

$$\tau = \tau_0 \exp(-E_t/kT),$$

where τ = free carrier life time and τ_0 is a constant, the exponential increase can thus be attributed to a trap depth of 0.049 eV

Steady-state photoconductivity and photoluminescence studies by Bhunia *et al* [6] had revealed the presence of an In donor with an activation energy of 0 040 eV which controlled electron lifetime at $T < 220$ K and a deep acceptor O_{Te} at an energy 0 404 eV above the valence band which determined the lifetime at $T > 220$ K. The steady-state photoconductivity showed a sharp maximum at 220 K compared with a maximum at 250 K for the transient studies It is thus evident that the presence of the In donor level accounts for the sharp increase in photoconductive decay time with increase of temperature between 210 K and 250 K, since it results in increase in effective free carrier lifetime. The quenching of photoconductivity above 220 K is due to the deep acceptor O_{Te} as explained earlier which could be passivated by H plasma treatment. It may be mentioned that ICP analysis had shown the concentration of In in ZnTe as 0.28 ppm and that of Cu at 0.042 ppm

It is observed from Table 1 that the decay time increased significantly with incident wavelength and the response amplitude also increased. This may be attributed to several reasons At photon energies at and above the band gap of 2.26 eV (548 nm) electron-hole pairs are created which can, on the cessation of the laser pulse, exhibit fast direct recombination as seen from Figure 1. At these energies

where α is reasonably high, absorption occurs near the surface With increasing wavelength α decreases and so the light penetrates deeper into the sample and hence, the role of surface recombination is reduced However, now absorption at lower-than-bandgap energies occurs due to excitation of electrons from filled acceptor levels above the valence band and hence, free holes are not created. This contributes to the increase of the free carrier lifetime of electrons in the conduction band Thus, the transient response at 585 nm (Figure 4) and 592 nm does not exhibit

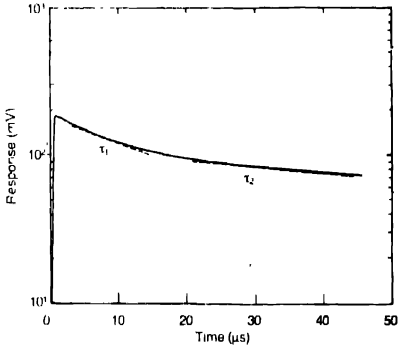

Figure 4. Transient photoconductivity with excitation at λ = 585 nm

the very fast decay due to direct recombination Comparing the transients at these two wavelengths, it is found that the amplitude of the response increases by a factor of 1 6 while the decay time increases by a factor of 1.5 Since the magnitude of photoconductivity depends on the $\mu\tau$ product, the increase in response amplitude can be attributed to the increase in free carrier life-time. The longer decay with time constant τ_2 is also seen to depend on the excitation energy and may be due to capture of electrons in shallow acceptors to restore equilibrium.

Ahrenkiel *et al* [8] have also shown by model calculations that the exact nature of the decay depends on the trap density as compared with the injection level Thus from Table 1, it is seen that the decay time depends on the incident light intensity, both τ_1 and τ_2 decreasing considerably at lower incident intensities This is because at higher injection levels, the occupancy of the traps is higher, leading to a lower rate of capture [9]

5. Conclusions

Direct determination of transient photoconductivity in Zn-annealed single crystal ZnTe was carried out by a contactless r.f technique using laser pulses at wavelengths of 532–592 nm The temperature dependence of the transient decay was explained on the basis of carrier trapping and excitation from a shallow In donor at a trap depth of ~0.04 eV The wavelength and intensity dependence of the photoconductive decay have also been studied

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